

PROBABILISTIC ASSESSMENT of GROUND-WATER VULNERABILITY to NONPOINT SOURCE POLLUTION in AGRICULTURAL WATERSHEDS

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Abstract

This paper presents a probabilistic framework for the assessment of ground-water pollution potential by pesticides in two adjacent agricultural watersheds in the Mid-Atlantic Coastal Plain. Indices for estimating streams vulnerability to pollutants' load from the surficial aquifer are also presented. The methodology combines physically based mass fraction models (or indices), which describe natural attenuation of pesticides in the subsurface with Monte Carlo simulations and ArcView GIS to generate pollution potential cumulative distributions in the soil for a selected pesticide. The pollution potential is defined here as the probability of exceeding a prescribed threshold limit of leached fraction of a pesticide's mass applied per acre at the source. Uncertainty of soil parameters, such as the saturated hydraulic conductivity, porosity, field capacity, and organic carbon fraction, are based on statistics and distributions related to drainage (SCS hydrologic) soil groups and soil texture. Probability density functions and cumulative distributions for the leached mass fractions below the root zone are generated through Monte Carlo simulations for different hydrologic soil groups and land use. The probabilistic scheme is applied to assess the vulnerability of ground water in two agricultural watersheds in the Mid-Atlantic coastal plain to a selected relatively short-lived pesticide. The probability maps and expected leached fractions of the pesticide show that well drained landscapes pose greater risks for potential ground water pollution by the pesticide. In the case of cultivated lands, the Monte Carlo simulations show that the coefficient of variation for the leached mass fraction is higher for poorly drained than in well drained soils in the area.

Introduction

Agricultural activities are the leading source of nonpoint source pollutants (NPS), which threaten sustainable agriculture and ground water and surface water resources (*Loague et al.*, 1998). Although pesticides are commonly present at low concentrations in ground water, they can have chronic impact on the environment and health. Methods are needed to predict in advance the fate and behavior of chemicals applied to the soil surface and whether they pose a threat to soil and ground water resources. Ground-water monitoring is too costly to adequately define the extent of the pollution problem at large watershed scales, and the cost involved in the cleanup of NPS is nearly impossible. It is becoming evident that researchers and regulatory agencies are increasingly relying on models to predict the transport and behavior of chemicals in the subsurface as well as surface waters, in order to anticipate in advance potential pollution problems. Ground-water vulnerability assessment methods may be classified into three general types: statistical methods, overlay index methods, and process-based transport models.

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Khan and Liang (1989) coupled the attenuation factor (AF) index with a GIS for mapping pesticide contamination potential in soils. Loague et al. (1995) and Diaz and Loague (2000) presented a GIS-based framework and first-order analysis for the assessment of the impact of data uncertainty on the leaching of NPS pollutants at the regional scale. Considering dispersive-reactive transport and separating the unsaturated zone into the root and intermediate-vadose zones, Hantush et al. (1999) presented first-order analysis with a GIS for the assessment of uncertainty of ground-water vulnerability to some pesticides in agricultural watersheds in the Mid-Atlantic coastal plains. Shukla et al. (2000) implemented the AF model with a GIS on a county scale to screen a group of pesticides.

In this paper a process-based index solute leaching model is integrated with a GIS to describe uncertainties (first-two moments) and probabilities of ground-water vulnerability in the Mid-Atlantic coastal plain to a selected pesticide in two agricultural watersheds. The index describes the leached fraction of the pesticide at depth in the subsurface. Potential extension of the framework to surface water vulnerability to ground-water discharge is also presented. The Monte Carlo simulations (MC) are used to generate the first-two moments and probability density and cumulative distributions of the mass fractions for different combinations of the hydrologic soil groups and land use. The integration of the MC results with a GIS allows for spatial display of models output and the interpretation of the results in relationship to landscape patterns, including soil hydrologic groups and land use.

Transport and Fate Models

Figure 1(a) depicts the soil-ground-water system under consideration, and Figure 1(b) shows potential pathway in the aquifer to the stream. When pesticides are applied to the soil surface, their leached fractions below the root zone may be described by the following equation (Hantush et al., 2000)

$$M_r = M_o \exp \left\{ -\frac{P_r}{2} \left[\sqrt{1 + 4 \frac{T_r}{P_r} \frac{\ln(2)}{\lambda_m} (1 + \mu + \phi_r)} - 1 \right] \right\} \quad (1)$$

where

$$\phi_r = \frac{\beta \alpha}{\alpha + \beta k_m R_{im}} \frac{k_{im}}{k_m} \frac{R_{im}}{R_m} \quad (2)$$

$$\mu = \frac{(FS + \sigma/h) \lambda_m}{\ln(2) R_m \theta_m} \quad (3)$$

in which M_r = the residual solute mass at the bottom of the root zone [M]; M_o = the initial mass applied per unit area at the soil surface, which is available for transport in soluble phase [M]; $P_r = h(q/\theta_m)/D_m$ is the soil root-zone Peclet number; $T_r = h R_m/(q/\theta_m)$ is the average residence time in the root soil [T]; q = the average flux per unit area in the root zone [L/T]; h = the depth of the root zone [L]; $\beta = \theta_{im} R_{im}/\theta_m R_m$; $k_m = \ln(2)/\lambda_m$ and $k_{im} = \ln(2)/\lambda_{im}$ are the degradation rates in the mobile and immobile phases, respectively [T⁻¹]; λ_m, λ_{im} = solute half-life in the mobile and immobile phase, respectively [T]; θ_{im} = the volumetric immobile water content; θ_m = the volumetric mobile water content; α = is the apparent mass transfer coefficient [T⁻¹] (i.e., mass transfer coefficient divided by R_m); $R_{im} = 1 + (f_{im} \rho_b K_d + \kappa_{im} K_H)/\theta_{im}$ is the retardation factor in

the immobile phase, in which f_{im} and κ_{im} are the fraction of soil bulk density and volumetric air contents in contact with the immobile water regions, respectively; $R_m = 1 + (f_m \rho_b K_d + \kappa_m K_H) / \theta_m$ is the retardation factor in the mobile phase, in which f_m and κ_m are the fraction of soil bulk density and volumetric air content in contact with the mobile phase, respectively; $D_m = (\kappa_m / \theta_m) K_H D_g^s + D_z$ is the effective (multiphase) dispersion coefficient in the mobile region [L^2/T]; in which $D_g^s = (\kappa_m^{10/3} / n^2) D_g^a$ is the soil gas diffusion coefficient [L^2/T]; n = soil porosity in the dynamic region (i.e., mobile phase); D_z = soil longitudinal dispersion coefficient [L^2/T]; μ = the volatilization and crop uptake loss parameter; $\sigma = K_H D_g^a / d$ is the vapor-phase conductance across the air-boundary layer on soil surface [L/T]; ρ_b = soil bulk density [M/L^3]; K_H = Henry's constant [dimensionless]; S = transpiration rate [T^{-1}]; F = transpiration-stream concentration factor; D_g^a = the binary gaseous diffusion coefficient [L^2/T]; and d = the thickness of air boundary layer on soil surface.

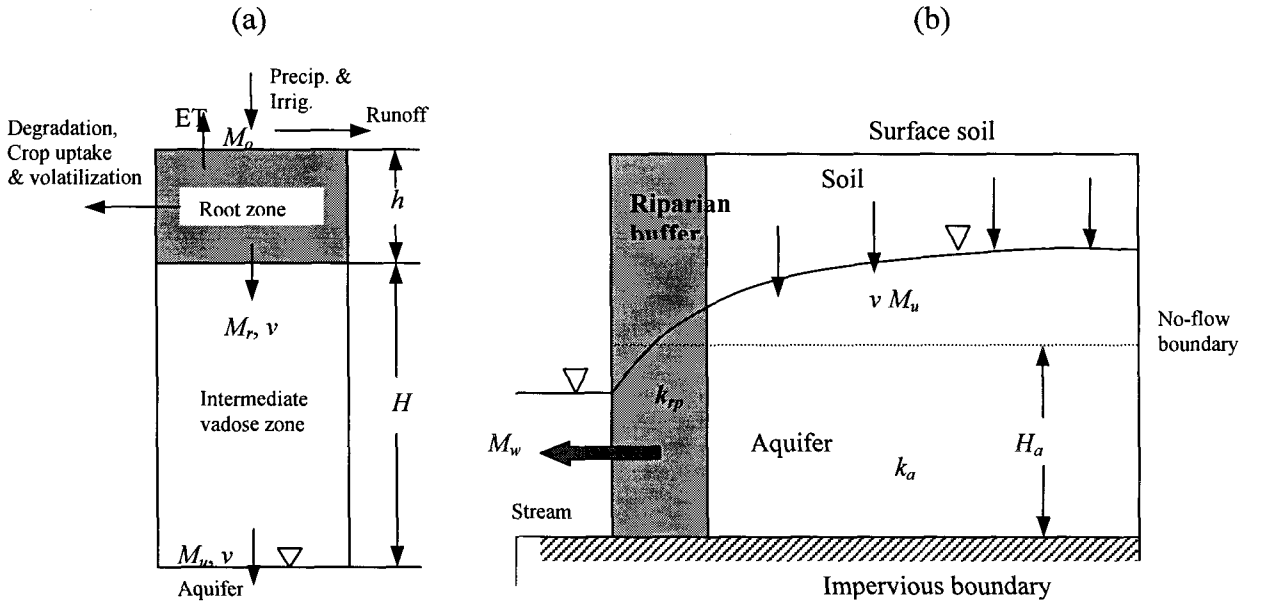


Fig.1 Schematic presentation of transport pathways: (a) soil-ground-water model, and (b) stream-aquifer system

Equation (1) is a modification of the leached-fraction expression of *Van der Zee and Boesten* (1991) for the effect of volatilization and lateral diffusive transfer in two-region soils. The extension of Equation 1, which describes leaching to the water table, M_u , is straightforward,

$$M_u = M_r \exp \left\{ -\frac{P_u}{2} \left[\sqrt{1 + 4 \frac{T_u}{P_u} \frac{\ln(2)}{\lambda_m} (1 + \phi_u)} - 1 \right] \right\} \quad (4)$$

in which P_u and T_u are defined similarly with H replacing h and v = net water flux below the root zone, replacing q . Other parameters are defined similarly, but for the vadose soil below the root zone. These models assume steady state flow in the soil and uniform soil property within each zone. Hydrologic and climatic input variables are considered on annually averaged basis in this effort. The effect of immobile-water phase is not considered since the soil data in the application

site does not provide sufficient information for meaningful mobile-immobile phase transport analysis ($\phi_r = \phi_u = 0$). A conservative scheme is implemented here in which pesticides losses below the biologically active root zone are ignored (e.g., *Rao and Hornsby*, 1991), in which case, emissions to the water table are given by $M_u = M_r$.

The moisture content in the root zone is assumed to be at field capacity (i.e., $\theta = \theta_{FC}$) and flow below the root zone is restricted to gravity drainage, $v = K(\theta)$, where $K(\theta)$ = the unsaturated conductivity as a function of the moisture content in the soil below the root zone (intermediate vadose zone) [L/T]. By using the model $K(\theta) = K_s (\theta/\theta_s)^{2b+3}$ (*Campbell*, 1974), the average moisture content in the intermediate vadose zone can be described by this relationship:

$$\theta = \theta_s (v / K_s)^{1/(2b+3)} \quad (5)$$

where K_s = the saturated-soil hydraulic conductivity [L/T]; θ_s = saturated-soil water content; and b is an empirical parameter (refer to *Clapp and Hornberger* (1978) for tabulated values of the parameters K_s , θ_s , and b for different soil textures).

Figure 2 illustrates the ground-water drainage, which is conceptualized in Fig. 1(b). It is assumed that the ground-water drainage coincides with the watershed drainage. If pesticides losses in the aquifer are negligible, the amount of a pesticide's mass discharged to the stream from the entire watershed, M_w , (Figs. 2) is the integral of net emissions to the water table, M_u , over the watershed area:

$$M_w = \iint_A M_u dA \quad (6)$$

in which, A = the area of the watershed excluding the riparian buffers [L²]. In the case of aquifer losses, one can show that the residual mass of the solute discharged to the stream, considering further losses in the riparian zone, is given by

$$M_w = \frac{\iint_A M_u dA}{(1 + T_a k_a)(1 + \xi T_{rp} k_{rp})}, \quad \xi = \frac{A_r}{A} \quad (7)$$

in which T_a and T_{rp} = the average residence time in the aquifer and the riparian buffer, respectively [T]; k_a and k_{rp} = first-order reaction rate in the aquifer and the riparian buffer, respectively [T⁻¹]; A_r = the area of the riparian buffer in the watershed. Note that, since $A_r \ll A$ (i.e., $\xi \ll 1$), greater value of k_{rp} will be needed as ground water flows through the riparian zone for natural attenuation to have any significant impact on the net mass discharge to the stream. Information on the degradation of pesticides in aquifers and riparian zones is scarce and half-life is commonly reported for soils only. In the example watershed of Fig. 2 (area outside the riparian buffer is agricultural), $\iint_A M_u dA \approx M_u^B A_B + M_u^C A_C + M_u^D A_D$, where $M_u^* = M_u$ estimated for the soil hydrologic soil group *.

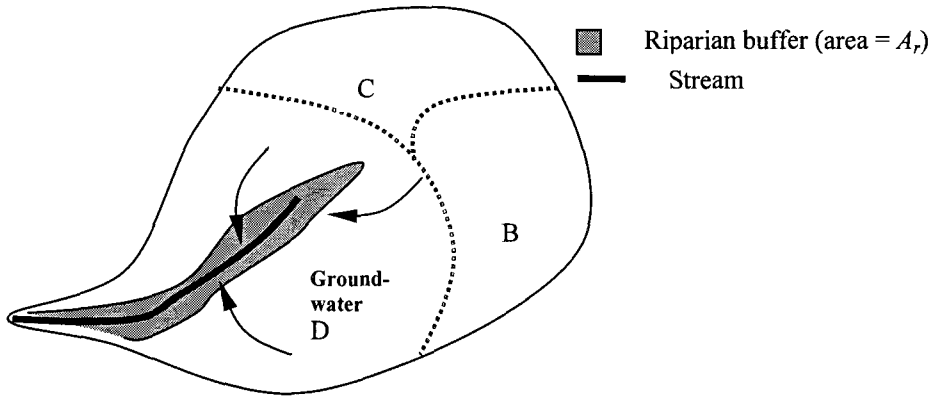


Fig. 2 Illustration of a watershed showing a stream, a riparian wooded area, and soils of hydrologic groups B, C, and D.

Study Site

The site consists of two adjacent agricultural watersheds of the Chester River Basin. The watersheds are located to the north of the Chester River in Kent County, Maryland. Morgan Creek and the Chesterville Branch drain both watersheds to the Chester River. 90 % of the landscape (Fig. 3a) is agricultural land and riparian wooded areas and orchards occupy much of the remaining portion. Corn, soybeans in and annual rotation with winter wheat are the major crops. The soil in this area ranges from loam to sandy and gravelly loam with the silt loam as the dominant texture. The soil in the Chesterville Branch is moderately well drained, of hydrologic group B, and in Morgan Creek it ranges from moderately poorly drained, C, to moderately well drained, B (Fig. 3b). The surficial aquifer is shallow and predominantly sand and gravel of fluvial origin. The extensive agricultural activities at the site coupled with the relatively shallow water table make the aquifer and the streams vulnerable to agricultural chemicals. Dicamba is among the most detected residues in the Delmarva Peninsula, and commonly used for Wheat-barley-alfalfa and Soybeans (Koterba *et al.*, 1993) and has the following chemical properties: $K_{oc} = 2.0 \times 10^{-3}$ (m^3/Kg), $K_H = 8.90 \times 10^{-8}$, and $\lambda = 14 \text{ d}$ ($k = 0.0495 \text{ d}^{-1}$).

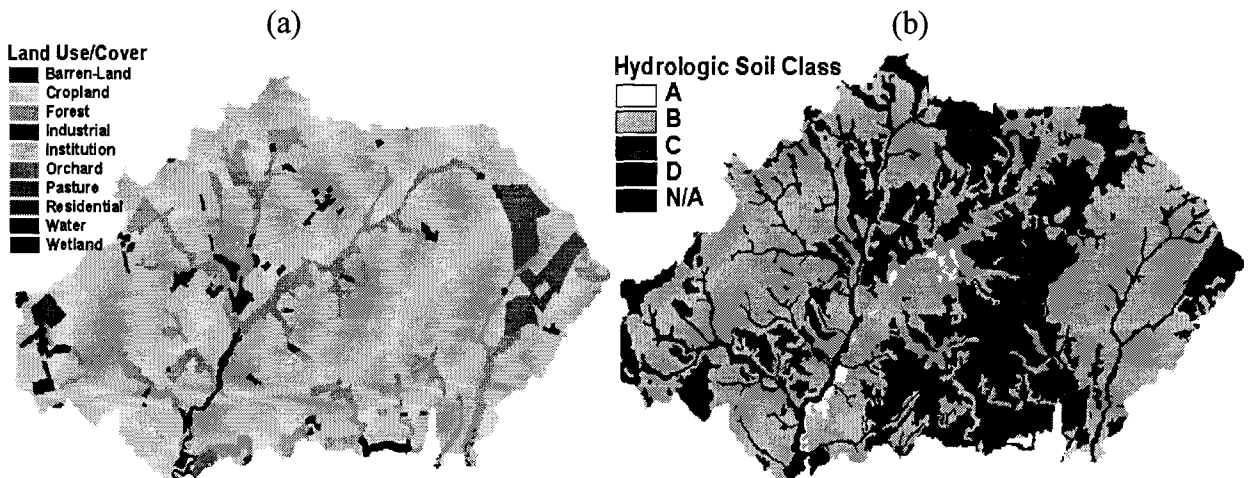


Fig. 3 Agricultural watersheds at the study site: (a) land use, and (b) soil hydrologic groups

The annual average flow in the root zone and net ground-water recharge are estimated based on the monthly water balance by subtracting runoff and evapotranspiration from the sum of precipitation and assumed values for irrigation (*Thorntwaite and Mather, 1957*). The runoff is estimated using the Soil Conservation Services (SCS) curve number approach based on combinations of hydrologic soil groups and land use. The evapotranspiration is estimated using a quasi-empirical method, which rely on energy balance and heat transfer and empirical crop factors.

ArcView GIS database is developed for the soil properties and land use characteristics using the soil survey of Kent County, Maryland (United States Department of Agriculture, Soil Conservation Service in cooperation with the Maryland Agricultural Experiment Station and the Kent Soil Conservation District, January 1982). *Carsel et al. (1988)* provide probability distributions for the soil parameters, among others, θ_{FC} , f_{om} , as a functions of hydrologic soil groups (A, B, C, and D) at soil depths (0.0-0.3 m, 0.30-0.60 m, 0.60-0.90 m, and 0.90-1.20). However, the distribution for the saturated hydraulic conductivity, K_s , and saturated moisture content, θ_s , were not reported based on this classification. Since generally different USDA soil textures corresponds to different hydrologic groups (e.g., group A corresponds to sand, loamy sand, and sandy loam), an attempt is made here to relate the statistics of K_s and θ_s based on soil texture to the corresponding Hydrologic group, and assuming that both soil properties, K_s and θ_s , are log-normally distributed. The probability distribution for each of the depth-averaged (over the root zone) soil properties, θ_{FC} , f_{om} , K_s , and θ_s , were based on statistics (mean and variance) derived for the depth-averaged property for each hydrologic group. Based on the empirical distribution, *Carsel et al. (1988)* suggested Johnson S_u distribution for θ_{FC} for the hydrologic groups B, C, and D,

$$Y = \sinh^{-1} (X/X_{UB}) \quad (8)$$

in which \sinh^{-1} = hyperbolic arc sine; X = original variable; and $X_{UB} = 0.6$ is the upper bound on field capacity. For the hydrologic group A, a lognormal distribution was used; i.e., $Y = \ln X$. Johnson S_B transformation is used to describe best the distribution of f_{om} ,

$$Y = \ln[X/X_{UB} - X] \quad (9)$$

in which $X_{UB} = 0.11$ as an upper bound on organic matter. Equations (8) and (9) transform θ_{FC} and f_{om} into normally distributed variables, respectively. The organic carbon fraction is related to organic matter by the relationship $f_{oc} = f_{om}/1.724$. The K_s and θ_s are considered log-normally distributed; i.e., $Y = \ln X$, where X is the original variable. The soil bulk density is assumed deterministic, because of low coefficient of variation (*Carsel et al., 1988*). The median values (equal to the mean values) were used to adequately represent bulk density. In this analysis, the variables are assumed statistically independent.

Monte Carlo Method

The Monte Carlo method is utilized to generate the probability distributions for M_r for the hydrologic soil groups (A, B, C, and D) and for different land use. The above distributions were utilized to generate 1000 random bits for each transformed variable. In each Monte Carlo simulation one set of the variables (θ_{FC} , f_{om} , K_s , and θ_s), from an ensemble of 1000 sets, is substituted into (1) to generate one value of M_r/M_o . This process was repeated for each distinct

and possible combination of hydrologic soil group and land use. Since we ignored decay below the root zone, $M_u = M_r$. In other word, the probabilistic scheme is a conservative one in which ground-water vulnerability is measured by M_r .

The hydrologic parameters, infiltration, u , ET , Runoff, and percolation below the root zone, v , are fixed at their annually averaged values in the MC simulations. To obtain more general distributions applicable for other pesticides used at the site, and associated with the hydrologic soil groups and land use, the approach is to repeat the Monte Carlo simulations for different values of the partition coefficient, K_{oc} , and half-life, λ , and then estimate the cumulative distributions by regressing on these parameters. However, this effort is not implemented here.

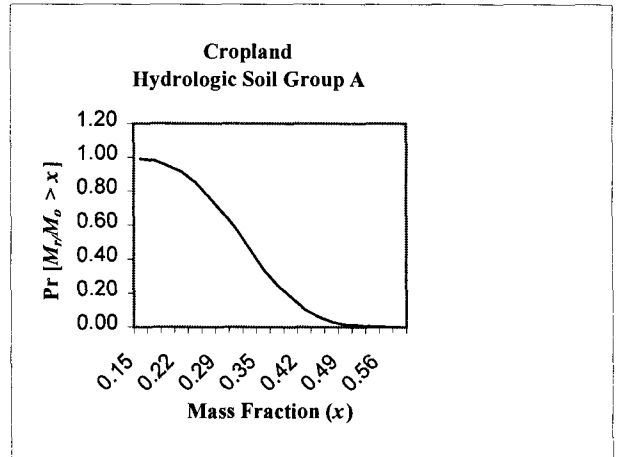
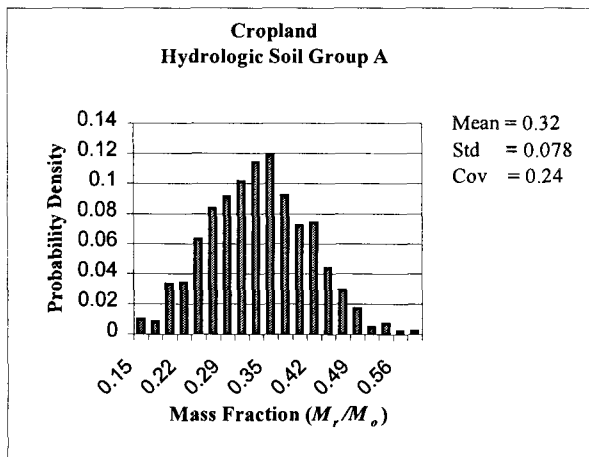
Figure 4 displays the results of the Monte Carlo simulations, the probability density function (pdf) and the cumulative distributions function (cdf) for the pesticide dicamba, associated with the hydrologic groups A, B, C and D, in agricultural fields. The pdf of hydrologic group A (well drained landscapes) is nearly normally distributed with significant probability density values for even relatively larger values of leached mass fractions; e.g., $M_r/M_o = 0.50$. The coefficient of variation of the leached fractions in this case is $Cov = 0.24$. The pdfs become increasingly skewed to the left toward smaller values of the leached fractions, M_r/M_o , as the soils become increasingly poorly drained, as Figure 4 shows. A remarkable observation here is that the coefficient of variation increases to $Cov = 0.786$ for the leached fractions in farmlands of hydrologic soil group D. That is, the lower leached fractions (associated with less vulnerabilities) show greater uncertainties, whereas for well drained soils, uncertainties of vulnerabilities are lower but with greater expected (or mean) leached fractions. The coefficient of variation for dicamba leached fractions is estimated to be similar in hydrologic soil groups B and C; $Cov = 0.32$ for B and 0.34 for C. At this site, the landscape is dominated by soils that fall in those two hydrologic groups, B and C. The mean vulnerability of ground water below farmland soils of hydrologic group B is estimated to be twice and a half greater than if the soil is of group C, but with almost similar level of uncertainty. The vulnerability of ground water in the Chesterville Branch watershed to dicamba is relatively higher than at Morgan Creek and with less uncertainty, because the landscape in the former is dominated by moderately well drained soils (B). The cumulative distributions (cdf) show that the probability of leached fractions to exceed a given threshold value decreases significantly from well drained to poorly drained landscapes. The probability of exceeding 0.42 value, $Pr[M_r/M_o > 0.42]$ is about 10 % for soil group A, which is high, although dicamba is short lived, half-life = 14 d. $Pr[M_r/M_o > 0.08]$ is about 0.6 for hydrologic soil group B and almost zero for group C.

Figures 5(a-c) show ArcView GIS maps for $Pr [M_r/M_o < 0.05, 0.1, 0.2]$, respectively. Note that one minus the displayed values corresponds to the probability of exceeding the leached fraction threshold value (0.05, 0.1, and 0.2). These maps do not reflect actual applications, but rather the vulnerability of the soil and ground water to potential application of a pesticide with characteristics similar to those of dicamba (e.g., dicamba may not be used in orchards). For the greater threshold value of 0.2, the areas that showed greater ground-water pollution risk (i.e., probability of exceeding 20%) are associated with pasture land, orchards, wooded areas along the creeks, and hydrologic soil group A, with the latter showing the highest risk. At this value of threshold, both soil groups B and C showed minimal vulnerabilities to leached fractions of the pesticide, except at areas of the above land uses. As the threshold value is reduced, the vulnerability map increasingly reflects the patterns of the land use and hydrologic soil groups in the area with significant probabilities (of exceeding threshold value). And at the lower threshold values of 0.1 and 0.05, the Chesterville Branch (soil group B) displays greater risk for potential

ground-water pollution than much of the eastern portion of Morgan Creek watershed (soil group C), with the exception of wooded areas along the northeast branch of Morgan Creek. Figure 5(d) shows that mean leached fractions of the pesticide. The orchard and wooded along the creeks show the greatest leached fractions, and wetlands and areas of soil group D show the lowest values. The standard deviations (Fig. 5 (e)), however, followed the soil drainage pattern more so than the land use, with greater values associated with moderately to well drained soils. The standard deviations associated with the leached fractions at the Chesterville Branch ranged from 0.02-0.04, except for lower values in some poorly drained landscapes.

Summary

A probabilistic framework was developed, using Monte Carlo simulations and ArcView GIS, for the assessment of ground-water vulnerability to potential pollution by pesticides. The Monte Carlo simulations were conducted to derive the probability density function and cumulative distributions of leached fractions of the pesticide dicamba below the root zone, using a process-based screening model. The methodology was applied to assess the risk for potential ground-water contamination in two agricultural watersheds in the Mid-Atlantic coastal plain by relatively short-lived pesticides with chemical characteristics similar to those reported for dicamba. The Monte Carlo simulations showed that farmlands with well drained soils may be at greater risk for ground-water pollution by the pesticide and with lower uncertainties than in poorly drained soils. The ArcView GIS probability maps showed that the probability of exceeding a given threshold value of leached fraction of the pesticide is related to the soil drainage characteristics of the landscape, including the hydrologic group and land use. Well drained landscapes showed the highest mean vulnerabilities and risk for exceeding the threshold value of assumed allowable leached fractions, including orchards, wooded areas along the creeks in the two watersheds, and pasture land. The estimated standard deviations followed the hydrologic soil groups rather than the land-use pattern, and with smaller values in the poorly drained landscapes. These results may have implication on the management of pesticides in agricultural watersheds.



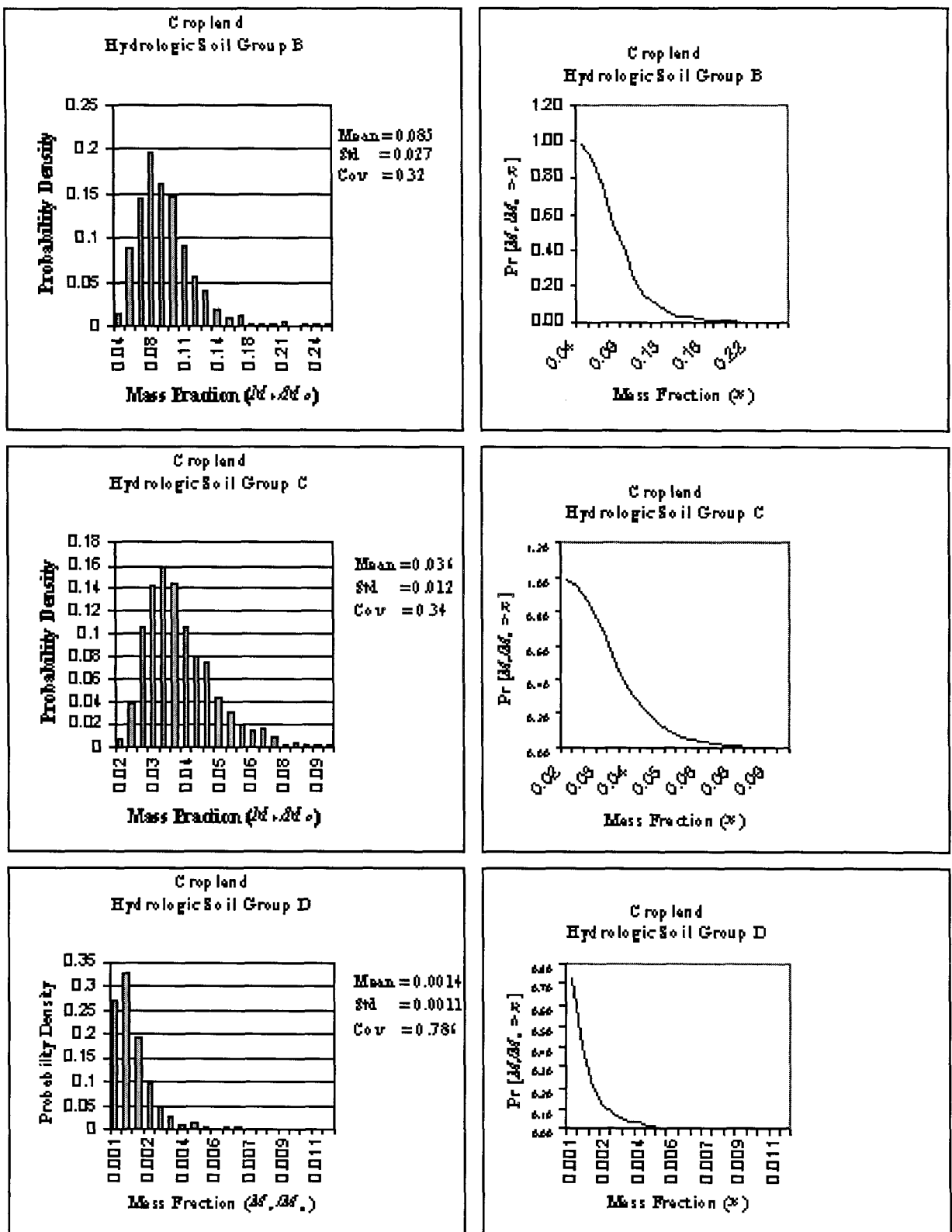


Fig. 4 Estimated probability density and cumulative distributions for the leached fractions, M_r/M_o , of dicamba for hydrologic soil groups A, B, C, and D in a typical cultivated land.

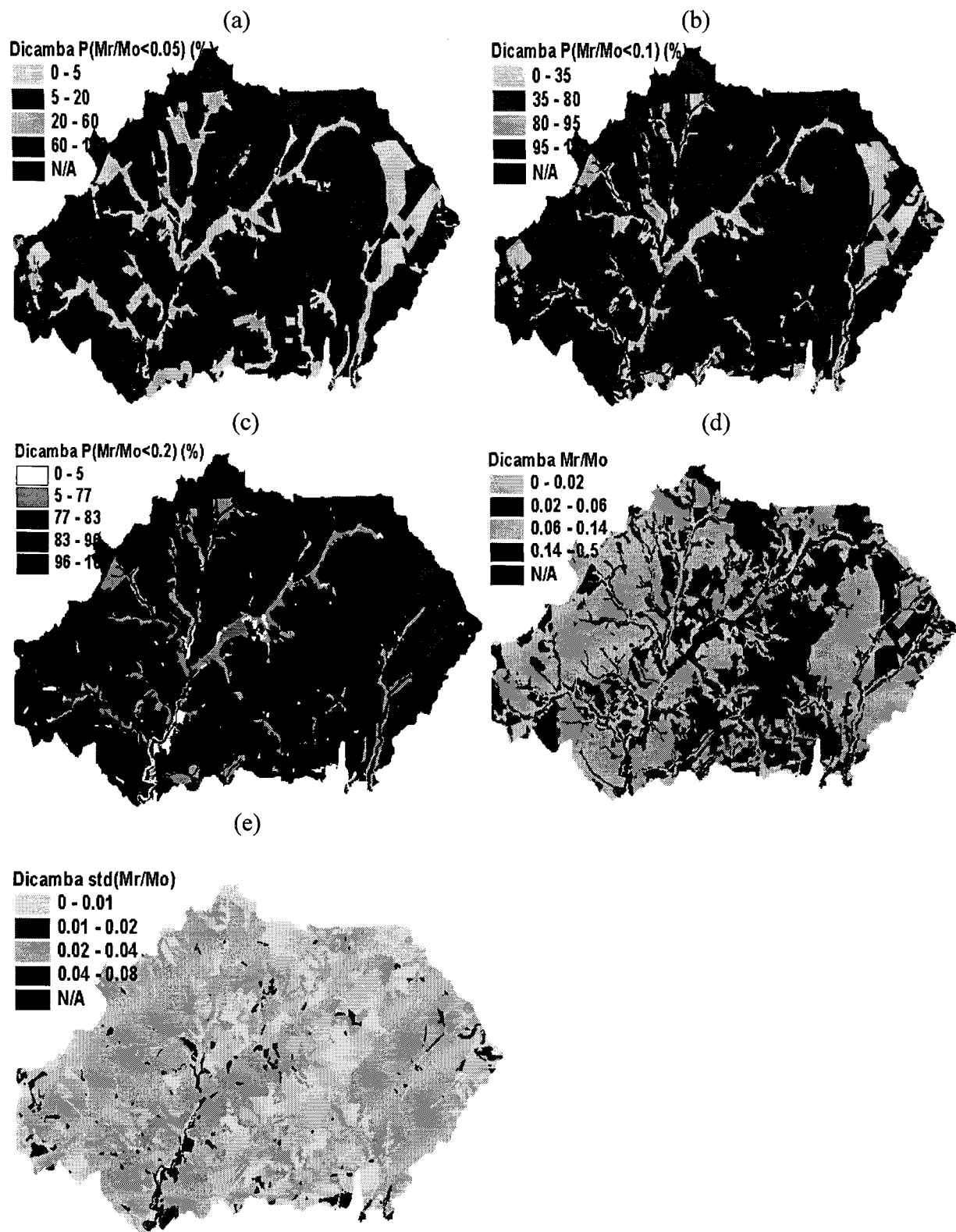


Fig. 5 ArcView GIS maps for $Pr[M_r/M_o < 0.05, 0.1, 0.2]$ and the mean and standard deviations of potential leached fractions of a pesticide similar to dicamba.

ACKNOWLEDGEMENT: *The U.S. Environmental Protection Agency through its Office of Research and Development funded and managed the research described here through in-house efforts. It has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency, and no official endorsement should be inferred*

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